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Master's Thesis

Design of polymeric binders
to enhance cycle stability of silicon anode
for Lithium ion battery

Sooham Park

Department of Chemistry

Graduate School of UNIST

2019

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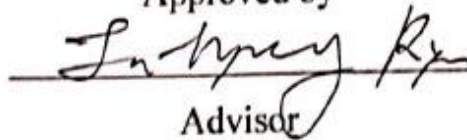
Design of polymeric binders
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A thesis/dissertation
submitted to the Graduate School of UNIST
in partial fulfillment of the
requirements for the degree of
Master of Science

Sooham Park

11/27/2018 of submission

Approved by


Advisor

Ja-Hyoung Ryu

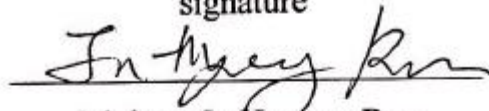
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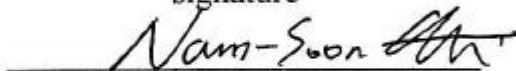
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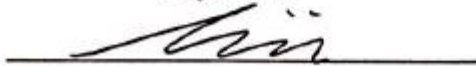
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Soojin Park

Abstract

With a variety of electronic device development, development of battery is under active. In addition, the importance of electronic car has come to the fore worldwide instead of car engine due to environmental pollution, so the development of high energy density and high capacity battery become more important for good mileage.

Lithium ion battery(LIB) is suitable battery to these requirements. Because LIB has high energy density compared to another battery and long cycle stability. Also it has high voltage which can make higher power. But conventional graphite battery has too low capacity to satisfy requirements. In order to increase the capacity of battery, high theoretical capacity materials are focused. One of promising material is silicon. Silicon has 10 times higher theoretical capacity compared to conventional graphite battery. But it undergo severe problems due to large volume expansion up to 300% during lithiation. If silicon cannot withstand its volume expansion, it become pulverization. And active material cannot stick to current collector leading to electrical isolation and cracks due to its volume expansion and pulverization. These problems make rapid capacity fading. Also almost anode material has solid electrolyte interphase(SEI) layer its surface at formation cycle. But SEI layer cannot withstand the volume expansion of silicon and it is broken. So exposed active material make SEI layer again and again. And this thick SEI layer make high resistance in electrode and show low cycle stability.

In this study, in order to solve these problems, we design two polymeric binder. Binder function like glue which can grasp and connect active material with current collector. First polymeric binder is double bond contained polymer. Double bond can undergo electrochemical reduction which can help make stable SEI. Another polymeric binder is azide group contained polymer. Azide can easily react with carbon defect. So with carbon coated silicon, we can make direct connection of active material with polymeric binder.

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Chapter I. Introduction of silicon anode and binder

1.1 Introduction of silicon anode

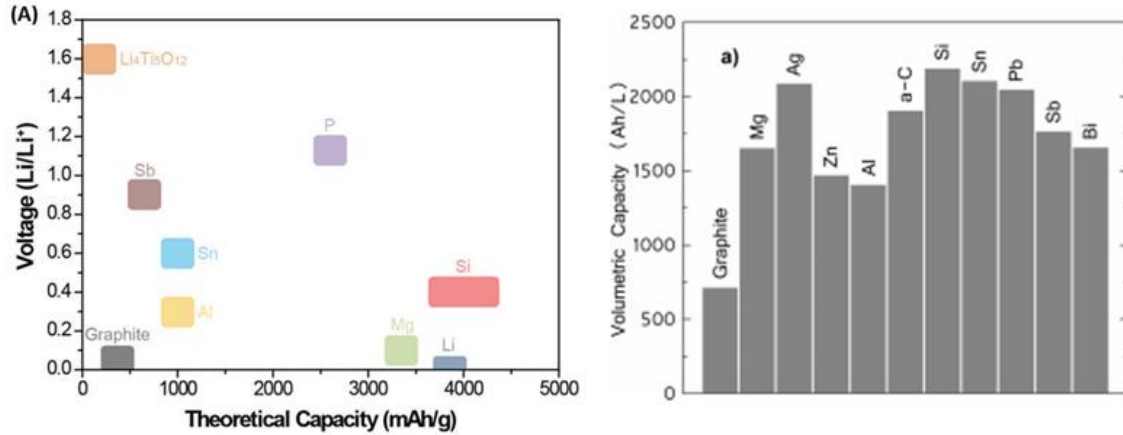


Figure 1.1 Theoretical capacity and volumetric capacity of various anode material ^[1,2]

Lithium ion batteries (LIB) is rechargeable secondary battery which can be repeatedly charged and discharged. LIB has many advantages compared to another secondary battery like high energy density, which can make battery downsizing, high voltage (about 3.7V) which can make high power for big power consumption product and longevity. With a variety of electronics development, the demand for high capacity of LIB increases. And in order to increase energy density, many researcher focus on new anode active material like aluminum, tin, lithium metal and so on. Figure 1.1 shows theoretical capacity and volumetric capacity of many promising active material for anode. Silicon anode material has been attracted because it has 10 times higher theoretical capacity than conventional graphite anode and highest volumetric capacity among these promising materials.^[3-5]

But silicon is hard to use as practical lithium ion battery, because it undergo severe problems. Silicon show volume expansion up to 300% during lithiation.^[6-9] Due to expansion, it has many problem such as delamination, unstable SEI and pulverization. In order to solve these problems, many researches have been done. One method is to make silicon as nano size such as nanowire, nanotube to overcome its pulverization.^[10-13] The other method is to make silicon as yolk shell structure to accommodate its large volume change.^[14-18] But these methods are hard to be practical because of high cost and low production yield.

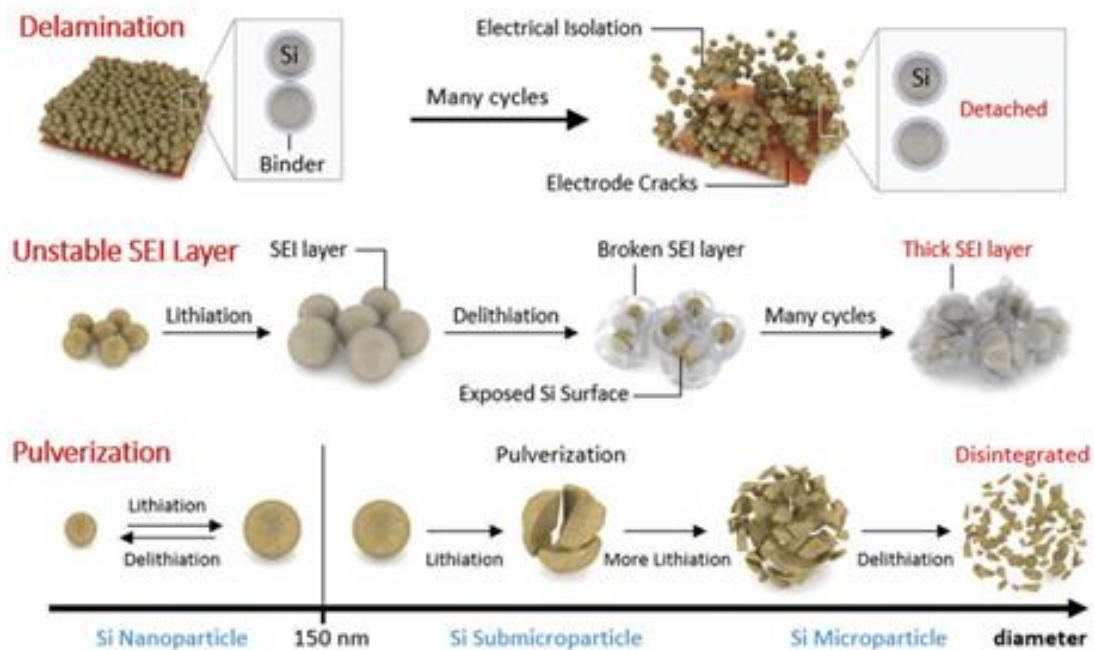


Figure 1.2 Schematic illustration of silicon problem due to silicon volume expansion ^[1]

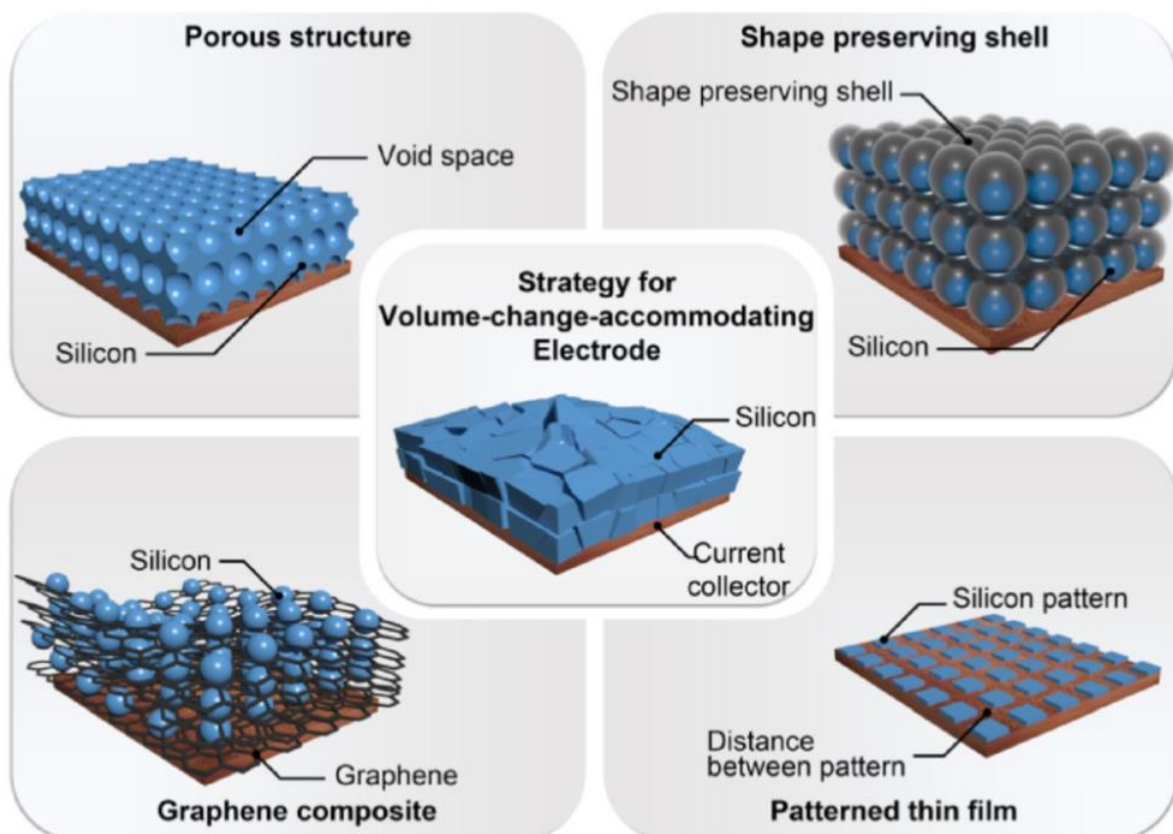


Figure 1.3 Schematic illustration of method to overcome silicon challenge ^[19]

1.2 Introduction of binder

Although binder is very small part in electrode, binder selection is important for stabilizing anode performance. And new binder synthesis is easier way to stabilize cycle stability compared to active material modification. For increase of capacity and energy density of electrode, people make much thicker electrode or choose new active material. But traditional binder, PVDF(Polyvinylidene fluoride), has lower interaction with active material, because it grasp active material by its van der Waals interaction which is too weak to bind hydrophilic silicon material.^[21] So it shows fast capacity fading. In order to enhance its cycle stability, many researcher synthesize and choose new polymeric binder. First, people select carboxyl group or hydroxyl group rich polymer to enhance the interaction between silicon and polymer and between silicon with current collector by its hydrogen bond and ion-dipole interaction.^[22] Many researcher try to use natural polymer like CMC(carboxymethyl cellulose) and guar, because these natural polymer have many hydroxyl group. And carboxylic acid group PAA, poly(acrylic acid), has high interaction with hydroxyl group of silicon. So these show enhanced cycle stability than PVDF. But these simple linear polymers are also insufficient for long cycle stability. So many researcher synthesized new polymer like branched-type for more strong interaction, crosslinking-type for 3D structure and covalent bond between polymer and hydroxyl group of silicon, self-healing type for recovering binder with silicon or binder with binder interaction based on hydrogen bond.^[23-25]

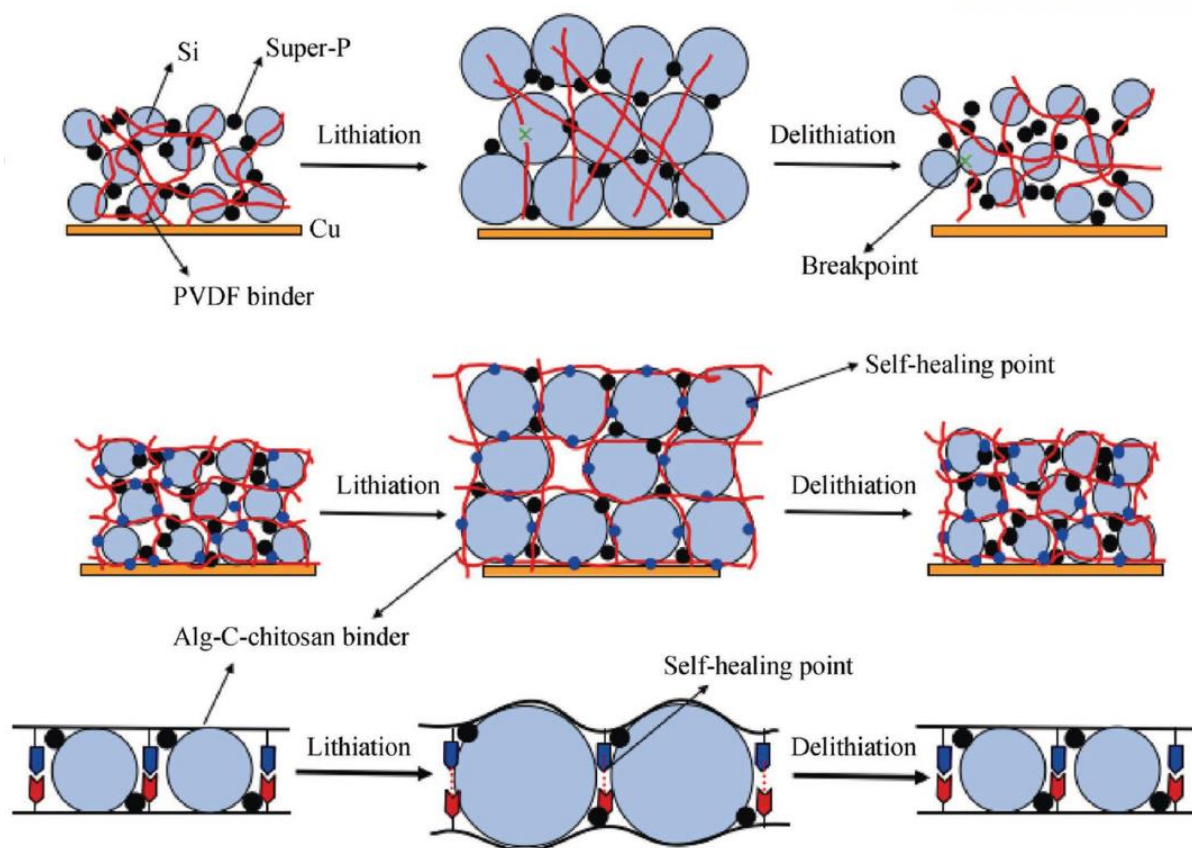


Figure 1.4 Difference between conventional linear binder with crosslinked self-healing binder ^[20]

Chapter II. Double bond contained polymer

2.1 Introduction

Silicon active material has been attracted because of its high capacity. But unstable solid electrolyte interphase (SEI) make poor cycle stability with continuous electrolyte consumption.^[26] SEI is made by reductive decomposition of electrolyte during lithiation on the surface of active material. In case of graphite anode, SEI is formed stably. But silicon which has high volume expansion break the SEI, and then the exposed surface of silicon make new SEI layer. During cycles, it gets more and more thick SEI which make high resistance in the electrode. To solve this problem, many methods have been developed like electrolyte additive which stabilize the surface of active material and surface coating to prevent SEI layer from making on the surface.^[27,28] In this study, we use double bond contained polymer as binder to help to make stable SEI layer. First, we bring double bond to poly(acrylic acid) which is suitable for silicon material because its rich carboxylic acid group can interact with hydroxyl group of silicon surface. And also, carboxylic acid group can crosslink with CMC. Second, we tested double bond with poly(lithium or sodium acrylate) which is more flexible than poly(acrylic acid).

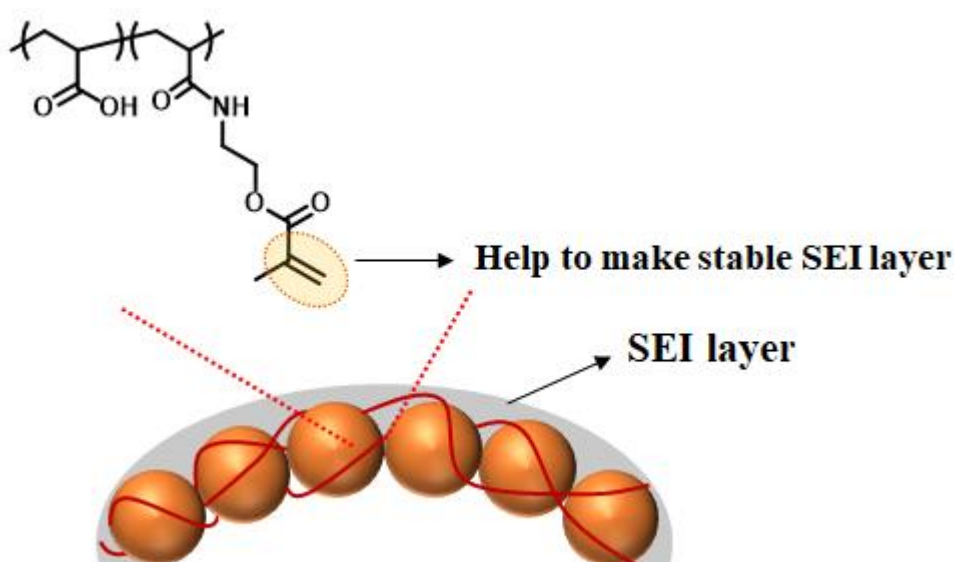


Figure 2.1 schematic description of double bond PAA in the electrode

2.2 Experimental

2.2.1 Materials

Poly(acrylic acid) solution(35wt%, MW ~100,000), 2-aminoethyl methacrylate hydrochloride were purchased from Sigma Aldrich, Korea. N,N-Diisopropylethylamine is purchased from Tokyo Chemical Industry(TCI), Tokyo, Japan. 3-(3-Dimethylaminopropyl)-1-ethyl-carbodiimide hydrochloride was purchased from CHEM-IMPEX INT'L INC., USA. HOBt anhydrous is purchased from GL Biochem(Shanghai) Ltd, China. Sodium hydroxide was purchased from Samchum pure chemical co., Korea. Lithium hydroxide monohydrate was purchased from Daejung chemical @ metals co., Korea.

2.2.2 Synthesis

Add poly(acrylic acid) solution(8g) to 250ml round bottom flask. Evaporate all water and then dissolve by DMF(100ml). Add EDC(690.6mg, 4.5mmol), HOBt(300.5mg, 2.2mmol), aminoethyl methacrylate(643.2mg, 3.9mmol) and DIPEA to solution. Stir 1day at room temperature. After dialysis, characterize by 400MHz ¹H-NMR and FT-IR spectroscopy.

After dissolve double bond PAA in water, add excess lithium hydroxide monohydrate or sodium hydroxide and stir 1day at room temperature. After dialysis to remove excess hydroxide, characterize by FT-IR spectroscopy.

2.2.3 Preparation of electrode

The electrode is prepared by casting slurry which composed of silicon nanoparticle, PAA based polymer, CMC and Super-P(silicon:PAA:CMC:Super-P=60:10:10:20) on copper foil. Electrode is dried in the oven at 80°C for 30min and then dry at 150°C in vacuum condition to remove water residue and to make crosslink between carboxyl group of PAA and hydroxyl group of CMC. With electrolyte consisted of 5wt% fluoroethylene carbonate and LiPF₆ (1.3M) in ethylene carbonate and diethylene carbonate(3:7 volume ratio), 2032 coin-type cells was assembly.

2.2.3 Electrochemical measurement

In order to check electrochemical stability, cyclic voltammetry is performed with polymer film. 5wt% polymer is casted on copper foil and assembled as 2016 coin-type cells. These are measured from 0.0V to 3.0V with 2mV/s scan rate.

Half-cells were tested in the voltage range of 0.005 to 2.0 V at 0.05 C for formation cycle and 0.005 to 2 V at 1 C for cycle performance. The cells were tested with WBCS-3000 battery cycler (Wonatech

Co.) at 25°C. And to figure out the rate capability of this polymer, it is tested at various charge rates(1C, 2C, 3C, 5C, 10C).

2.3. Result and Discussion

2.3.1 Double bond contained polymer synthesis and characterization

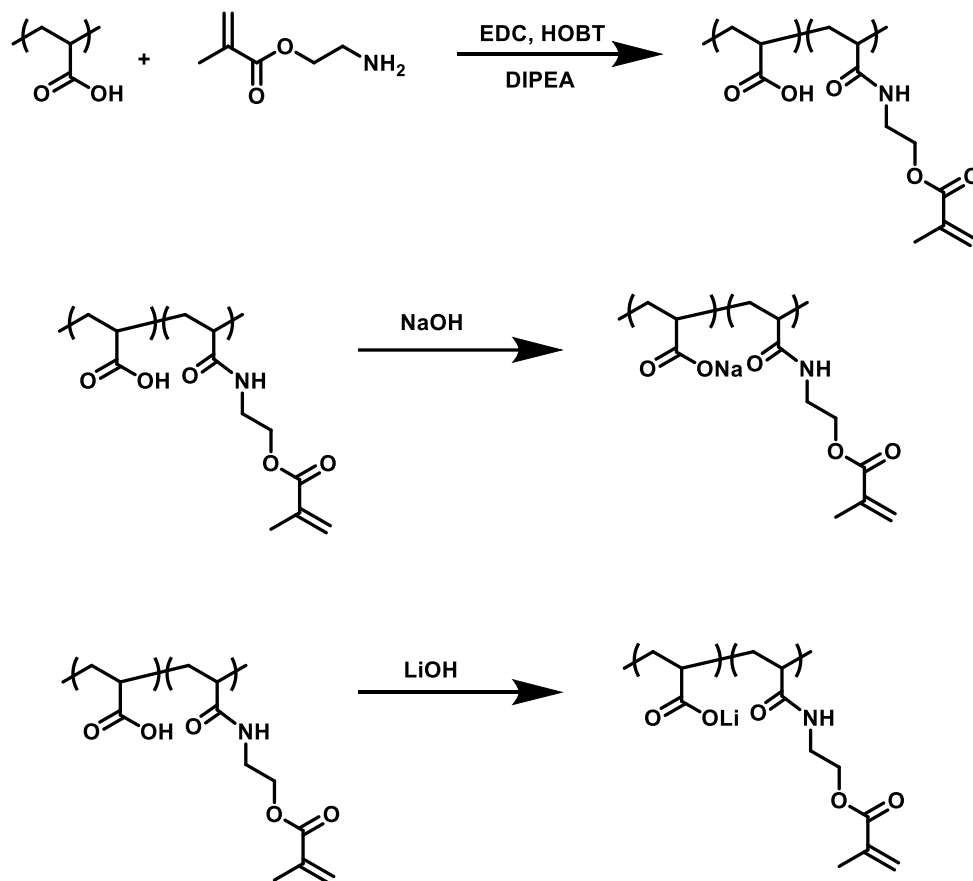


Figure 2.2 Double bond polymer synthesis schemes

Double bond PAA is easily synthesized by EDC coupling of carboxylic acid group of PAA with amine group of aminoethyl methacrylate. And synthesized polymer is confirmed by H-NMR, Figure 2.3, and FT-IR, Figure 2.4. H-NMR show protons of double bond (5.64ppm, 6.06ppm) is well conjugated to PAA but it is hard to see how much double bond is connected because most peaks are overlapped. FT-IR not only can make qualitative analysis but also show the amide bond (1640cm^{-1}) by EDC coupling of double bond. Poly(acrylic acid) can be easily change to poly acrylate by adding excess sodium or lithium hydroxide. After change poly(acrylic acid) to poly(lithium or sodium acrylate), IR show the change of peak carboxylic acid to carboxylate. C=O stretch (1713cm^{-1}) and C-OH (1251cm^{-1}) stretch peaks of carboxylic acid is reduced and symmetric (1403cm^{-1}) and asymmetric stretch (1555cm^{-1}) peaks of COO^- appear.

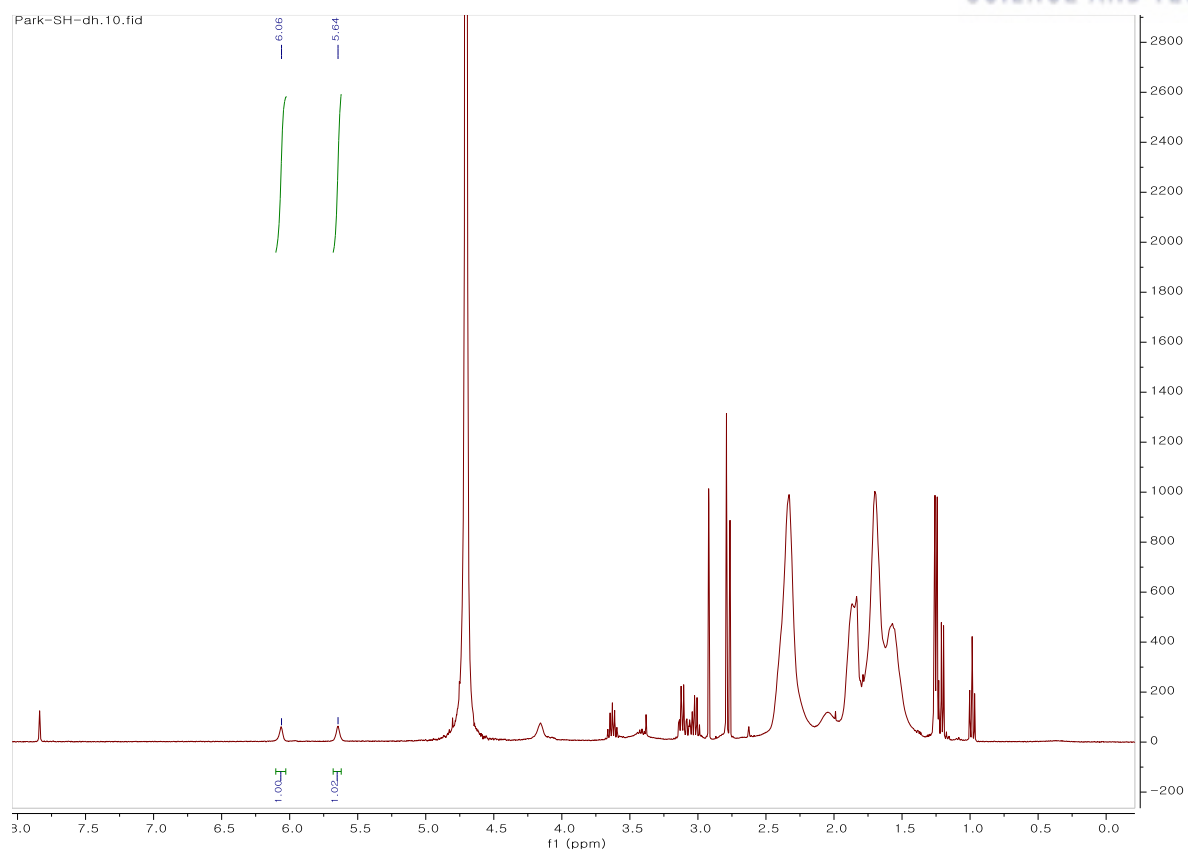


Figure 2.3 ^1H -NMR spectrum of double bond contained poly(acrylic acid)

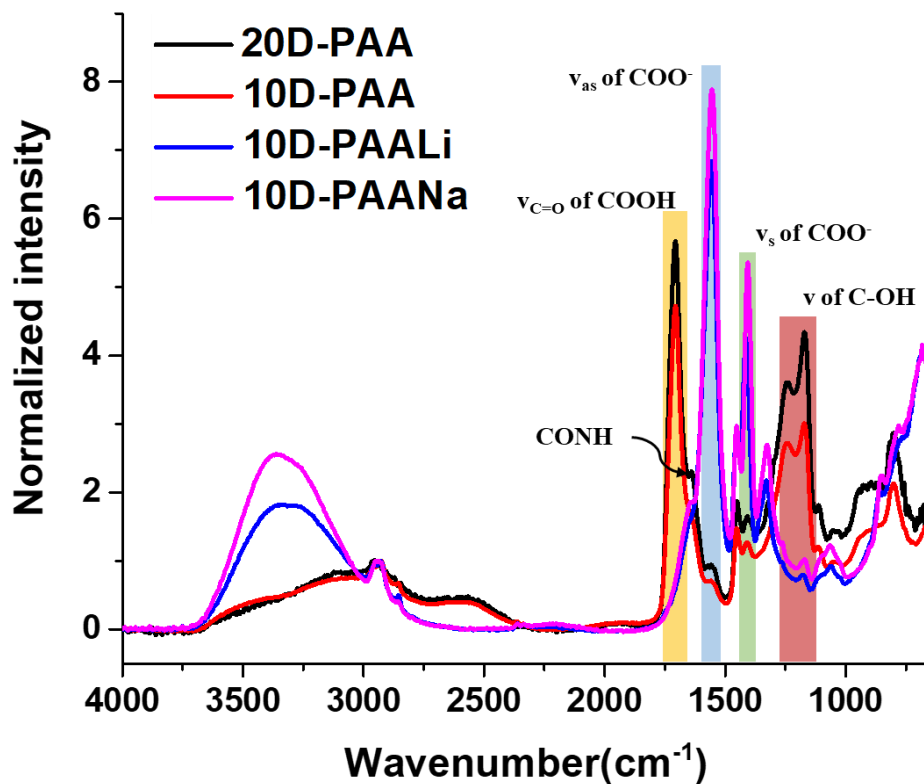


Figure 2.4 FT-IR spectrum of double bond contained poly(acrylic acid) and polyacrylate

2.3.2 Electrochemical performance

Before testing the electrochemical performance, cyclic voltammetry is tested for electrochemical stability in the voltage range from 0.01V to 3V. Figure 2.5 shows the cyclic voltammetry of PAA as reference with new double bond polymers. These all polymers show very small current range during charge-discharge cycle. When we see the data at milli ampere, there all polymer samples show same current property. Although double bond polymer show a little high current range, these polymers show micro ampere current scale. So side reaction of these new polymer is a negligible quantity and these polymers can be acceptable as binder.

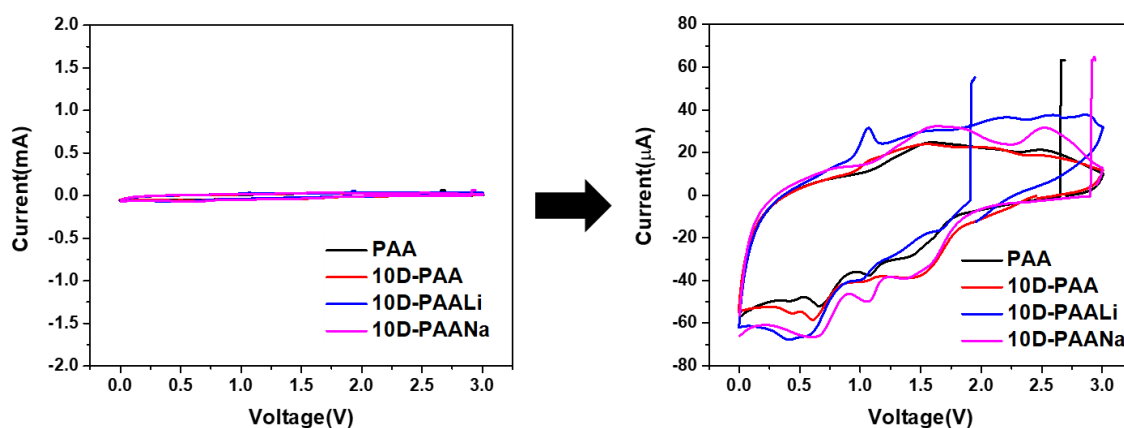


Figure 2.5 Cyclic voltammetry of PAA, 10D-PAA, 10D-PAALi, 10D-PAANa polymer film

We set reference polymeric binder as PAA/CMC. Figure 2.6(a) is the voltage profile of initial cycle. These electrodes have similar initial coulombic efficiency (ICE) (PAA: 85.2%, 10D-PAA: 85.2%, 10D-PAANa: 84.6%, 10D-PAALi: 87.2%) but lithium polyacrylate show low initial capacity compared to polymer electrodes because after formation cycle, lithium polyacrylate show higher impedance. And double bond poly(acrylic acid) and sodium acrylate show similar impedance with reference electrode (Figure 2.7). In terms of cycle stability, these polymers show almost similar cycle retention (Figure 2.6).

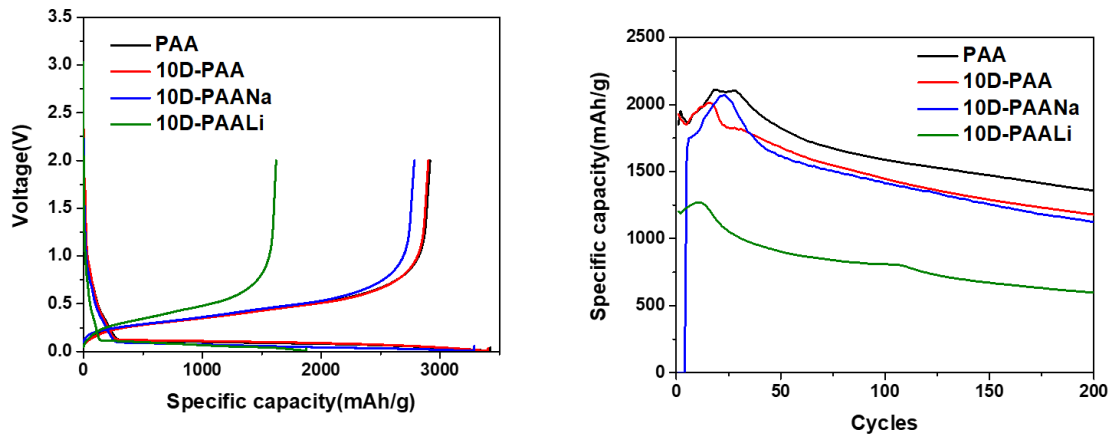


Figure 2.6 Electrochemical performance PAA/CMC reference and double bond contained polymers

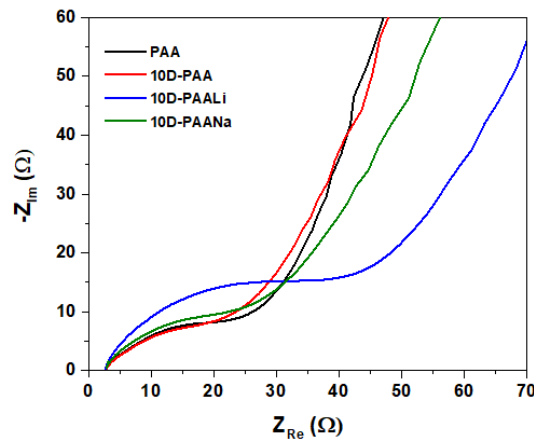


Figure 2.7 Impedance of PAA/CMC reference and double bond contained polymers

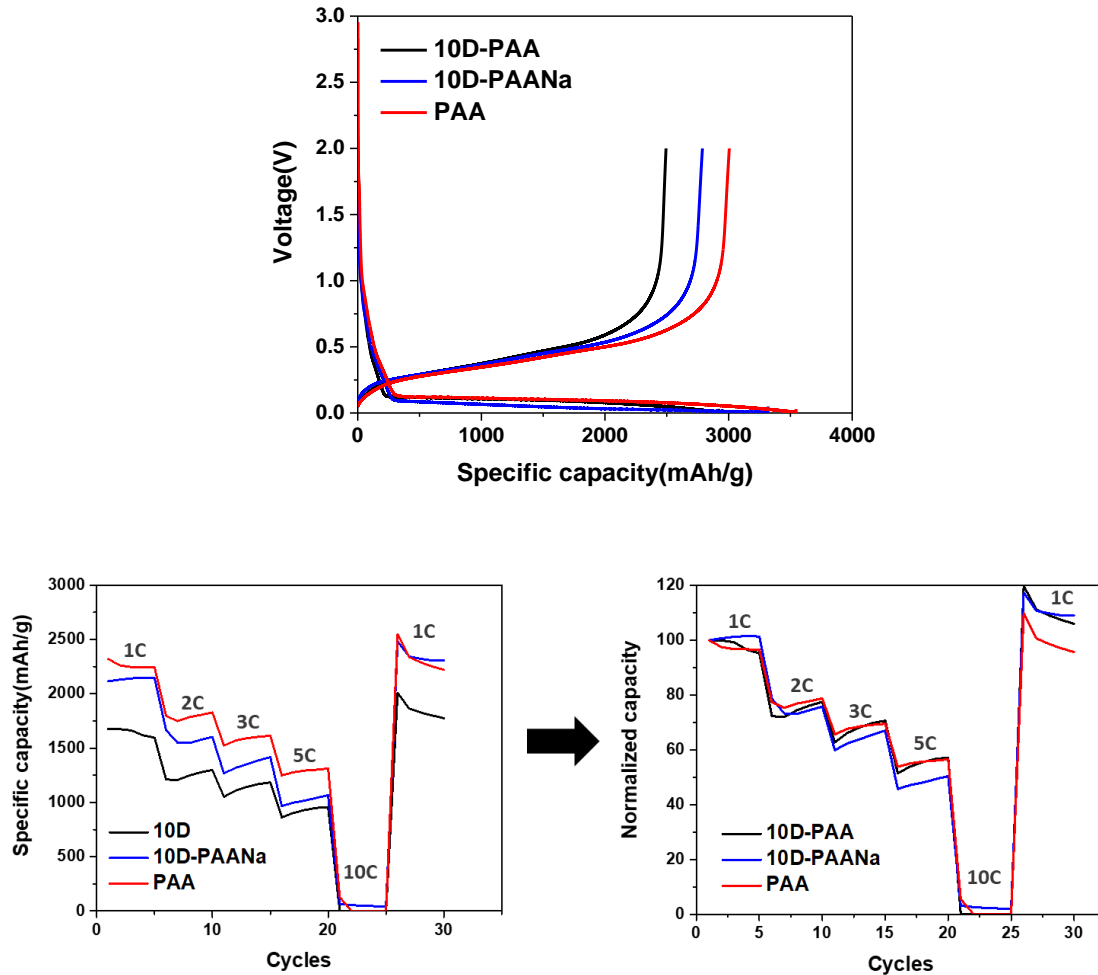


Figure 2.8 Rate performance with various C-rate

Figure 2.8 is rate capability of electrodes with various current rates of 1.0, 2.0, 3.0, 5.0 and 10 C-rate. After formation cycle, in order to stabilize the surface of electrode, we made 15 cycle performance at 1 C-rate. Although these all electrodes show similar property with increased rate, after come back to 1.0 C-rate, double bond contained polymeric binders show more high charge reversibility. In order to analysis this property, we see the impedance of these electrode after formation and after rate test (Figure 2.9). Before rate performance, these electrodes show similar impedance. But after rate performance, double bond contained poly acrylate show similar impedance with before performance. And it is very small resistance compared to reference.

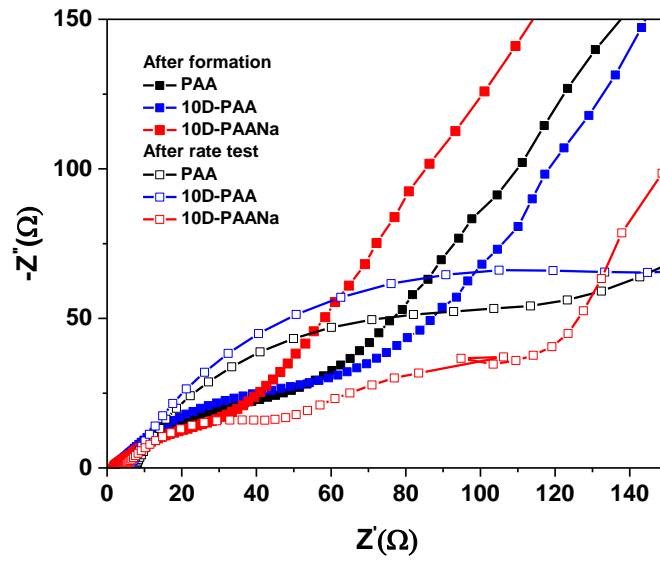


Figure 2.9 Impedance of after formation cycle and after rate performance

2.3.3 Surface morphology

In order to investigate the electrochemical performance of polymers, we observed the surface morphology by using rate performance(45cycles) cells. Rate test show the all polymer electrodes have similar cycle property but double bond contained polymer have high capacity reversibility. Especially double bond with acrylate polymer show the biggest reversibility with high specific capacity. SEM images show the PAA cannot maintain the integrity of electrode with many cracks on surface. Also, it show severe electrode aggregation. In case of 10D-PAA, although it also has many cracks on the surface of electrode, it has less aggregated particles. Compared to these electrodes, acrylate electrode show smaller and no significant cracks on surface by maintaining the stable integrity.

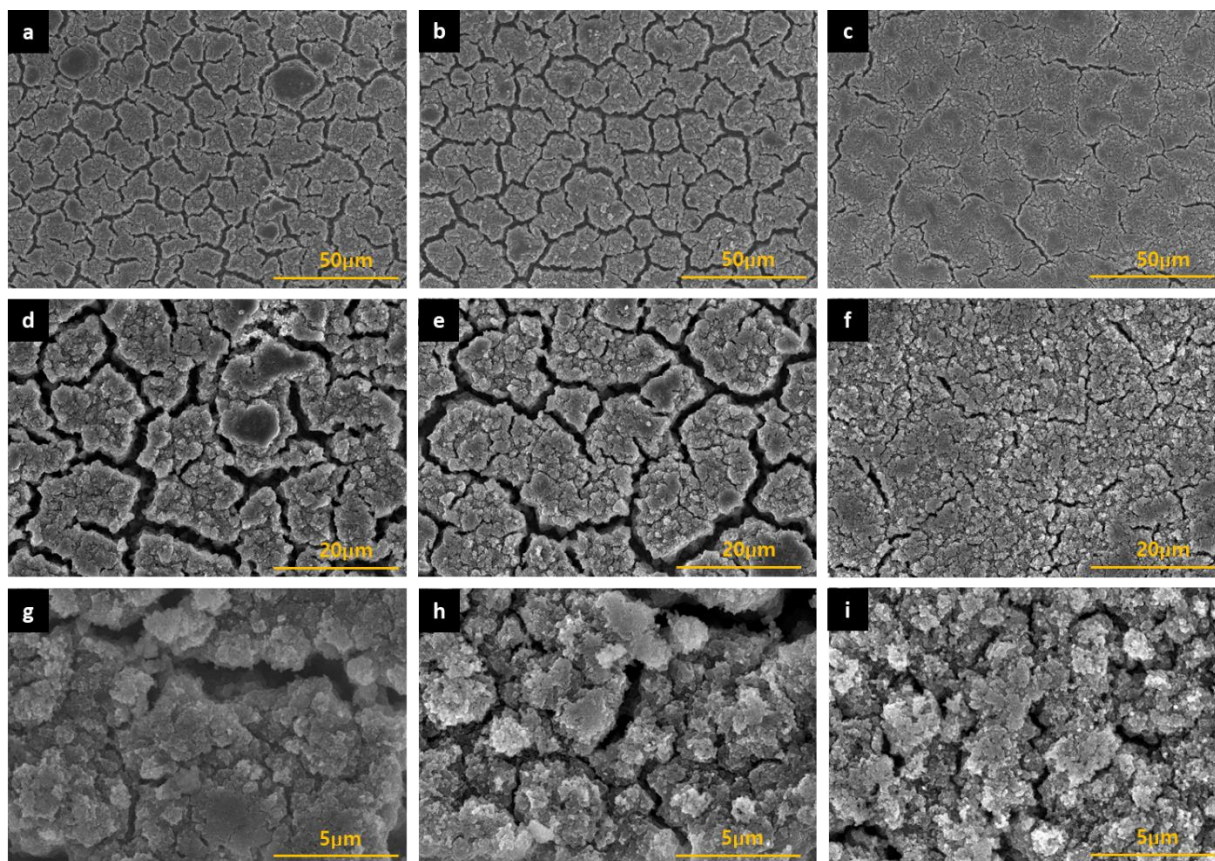


Figure 2.10 Surface morphology of electrodes after rate test (45cycles) by Scanning Electron Microscopy [a, d, g : PAA] [b, e, h : 10D-PAA] [c, f, I : 10D-PAANa]

In conclusion, we successfully synthesized double bond contained polymer based on poly(acrylic acid) which can make crosslink with CMC binder and is suitable for silicon anode. We confirmed the synthesis by NMR and FT-IR. It has electrochemical stability at LIB working voltage. Although it has no significant enhanced cycle life, it has high capacity reversibility in rate performance due to its low impedance. The surface morphology shows that double bond can prevent the severe electrode aggregation and acrylate polymer shows the good cycle data with stable electrode integrity.

Chapter III. Azide contained polymer

3.1 Introduction

Si-based Li ion battery anodes have attracted because of its high capacity. But its high volume change adversely affects battery performance. So binder selection is important for stabilizing anode performance. Traditional binder has lower interaction with active material. During charge and discharge, it lacks binding ability. Here, we prepared new polymeric binder which can make directly covalent bond with electrode composites. By using this new binder which have azido group, we can make crosslinked electrode with high mechanical strength. It is well known that azido group easily decomposes to nitrene by heat or UV treatment. And nitrene has high reactivity with C-H and C=C bonds. So by using this binder, it can connect and crosslink active material and give high mechanical strength. Connecting binder with active material can prevent active material from electrical isolating and will make high stability and efficiency during long cycle.

Also, azide group can react with carbon nanotube by same method, nitrene chemistry. Carbon nanotube(CNT) is well known as its high electronic conductivity and high mechanical strength. By connecting active material and CNT with polymer, this electrode can maintain its conductivity during long cycle and also CNT give integrity with mechanical strength to electrode.

In this study, we prepared electrodes with two methods to exploit the property of azide functional group. First is making electrode by UV treatment. Second is making electrode with CNT.

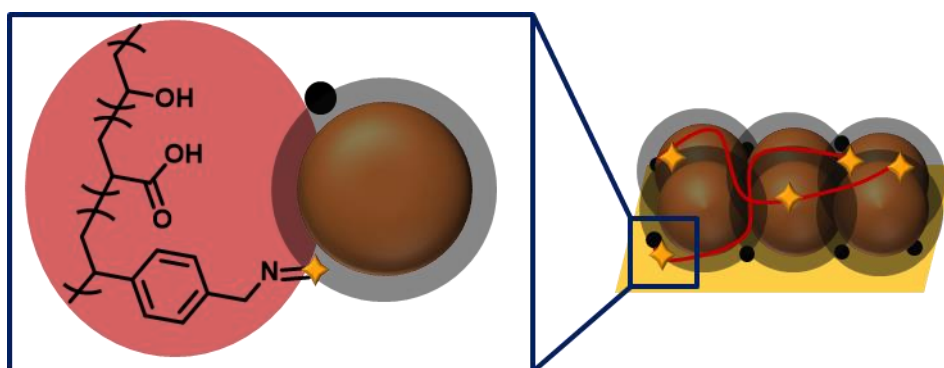


Figure 3.1 Schematic illustration of electrode with azide group contained polymeric binder

3.2 Experimental

3.2.1 Materials

Methyl acrylate(stabilized with MEHQ), Sodium azide were purchased from Tokyo Chemical Industry(TCI), Tokyo, Japan. 4-Vinylbenzyl chloride and aluminum oxide were obtained from Sigma Aldrich, Korea. Potassium hydroxide was purchased from Samchum pure chemical co., Korea.

3.2.2 Synthesis

Methyl acrylate was filtered with aluminum oxide for removing inhibitor. AIBN (2mg), 4-vinylbenzyl chloride (0.046g, 0.3mmol) and methyl acrylate (2g, 23mmol) were added to 25ml round bottom flask. After close the flask by rubber septum and parafilm, purge with Ar gas for 1hour. And then stir 1day at 70°C. Solve polymer in THF and precipitate in water three times. The polymer was characterized by using 400MHz H-NMR and GPC. After dissolve polymer in DMF, add sodium azide (97.5mg, 1.5mmol). Stir 3h at 45°C and then precipitate in water. Polymer is characterized by 400MHz H-NMR and FT-IR spectroscopy. Dissolve polymer by THF and then add potassium hydroxide for deprotection. After stir 3days, there is separated solid polymer. Dissolve polymer in water and purify by dialysis. Characterize the polymer by 400 MHz H-NMR and FT-IR spectroscopy.

3.2.3 Polymer coating to active material

Polymer and carbon coated silicon nanoparticle(100nm) are mixed for 30min. After casting mixed slurry on the glass, dry water for 1h at 80°C. Treat 254nm UV with 6W power for 1h with blocking external light at a distance 4cm. To remove polymer which is not interact with silicon nanoparticle, pour UV treated slurry into centrifuge tube and add 30ml of water. Stir at 12000rpm for 10min by ultracentrifuge and dispose supernatant by plastic pipette. Repeat 3 times and remove water by freeze dryer during 2 days. Characterize silicon by TGA with N₂ gas. TGA is performed with 5°C/min rate up to 600°C.

3.2.4 Preparation of electrode with polymer coated silicon

The electrode is prepared by casting slurry which composed of polymer coated silicon nanoparticle, Super-P(polymer coated silicon:Super-P=9:1) on copper foil. Electrode is dried in the oven at 80°C for 30min and then dry at 150°C in vacuum condition to remove water residue. With electrolyte consisted of 10wt% fluoroethylene carbonate and LiPF₆ (1.3M) in ethylene carbonate and diethylene

carbonate(3:7 volume ratio), 2032 coin-type cell was assembled.

3.2.5 Preparation of electrode with SWCNT

Add polymer(150mg) to 0.1wt% and 0.2wt% single walled carbon nanotube(SWCNT) solution(15g) and make homogeneous solution by vigorous stirring. Make electrode slurry with ratio 8:1:1:0.1/0.2(active material : Super-P : polymeric binder : SWCNT) and cast on copper foil. It is dried in the oven and 2032 coin-type cell was assembled with electrolyte (10wt% fluoroethylene carbonate and LiPF_6 (1.3M) in ethylene carbonate and diethylene carbonate(3:7 volume ratio)).

3.2.7 Electrochemical measurement

In order to check electrochemical stability, cyclic voltammetry is performed with polymer film. 5wt% polymer is casted on copper foil and assembled as 2016 coin-type cells. These are measured from 0.0V to 3.0V with 2mV/s scan rate.

Half-cells were tested in the voltage range of 0.005 to 1.5 V at 0.05 C for formation cycle and 0.01 to 1.2 V at 1 C for cycle performance. The cells were tested with WBCS-3000 battery cycler (Wonatech Co.) at 25°C.

3.3. Result and Discussion

3.3.1 Azide contained polymer synthesis and characterization

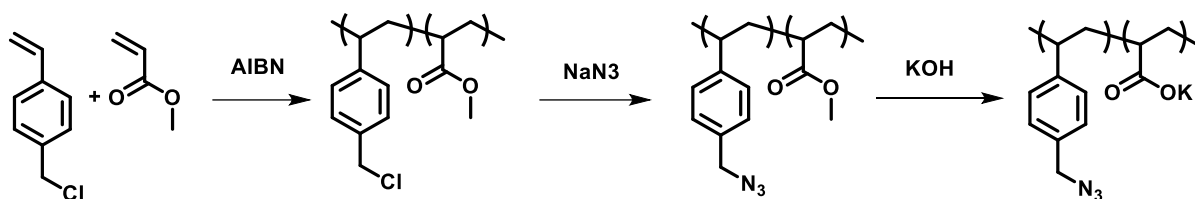


Figure 3.2 Synthesis scheme of N3-PAAK

Azide polymer is synthesized by free radical polymerization of 4-vinylbenzylchloride and methyl acrylate. Azide is used to connect polymer with active material. So with high azide ratio polymer, the surface of active material can get more connected polymers because polymer has many reaction site. After conjugation azide to benzyl chloride, NMR and FT-IR can prove the change of benzyl chloride to azide. Compared to Figure 3.3 (a) and (b), there is benzyl group shift 4.56ppm to 4.30ppm due to azide conjugation. And also, we can calculate the ratio of copolymer by using benzyl azide peak (4.30ppm) and methyl of methyl acrylate (3.66ppm) in Figure 3.3 (b). After deprotection by potassium hydroxide, Figure 3.3 (c) show no methyl peak. And we can see the functional group of final product by FT-IR(Figure 3.5). Figure 3.5 show azide peak at 2106cm^{-1} and asymmetric stretch peak of potassium acrylate at 1556cm^{-1} due to potassium hydroxide. And we synthesized two different ratio of azide polymer in order to see the effect of azide and crosslink amount. GPC data in Figure 3.4 shows that two polymers have similar molecular weight around 35k Da.

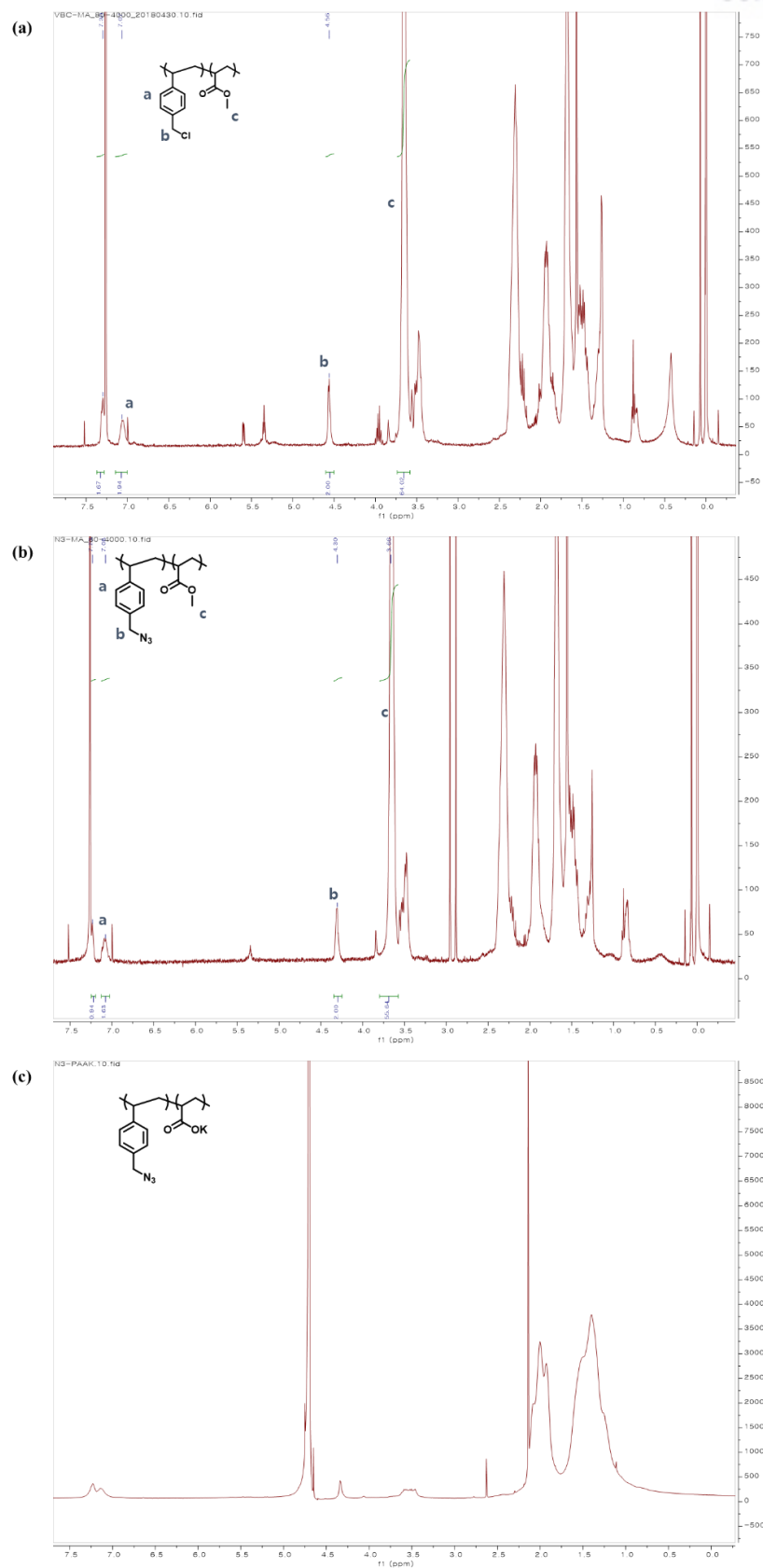


Figure 3.3 ^1H -NMR spectra of synthesis procedure of N3-PAAK

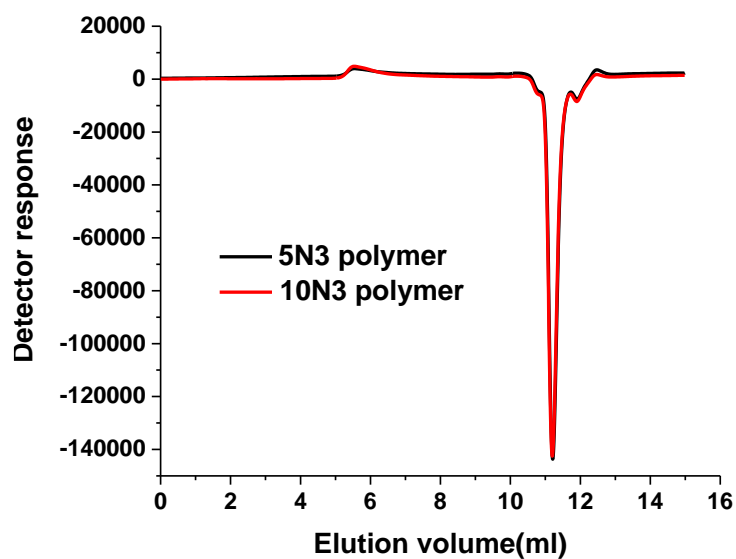


Figure 3.4 GPC peak data of different azide ratio polymer

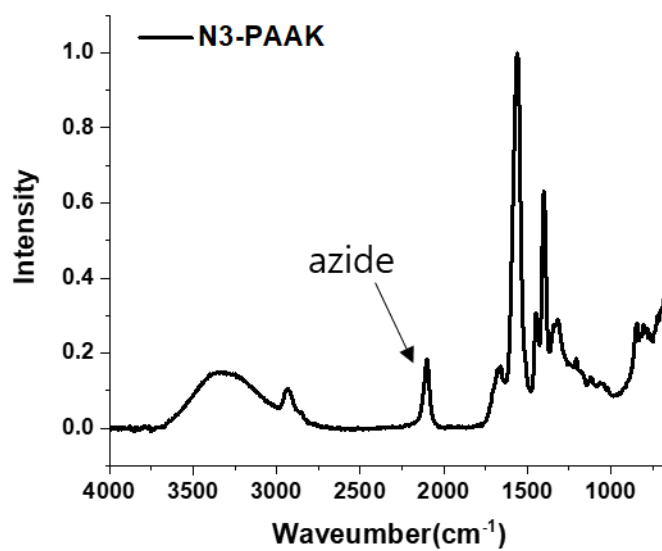


Figure 3.5 FT-IR spectrum of azide polymer

3.3.2 Electrochemical performance

Before testing electrochemical performance, cyclic voltammetry is tested for electrochemical stability in the voltage range from 0.01V to 3V. Figure 3.6 shows the cyclic voltammetry of PAA as reference with different ratio of azide polymers. These all polymers show very small current range during charge-discharge cycle. Although azide is a little large current than PAA reference, it is also very small. So side reaction of these new polymer is a negligible quantity and these polymers can be acceptable as binder.

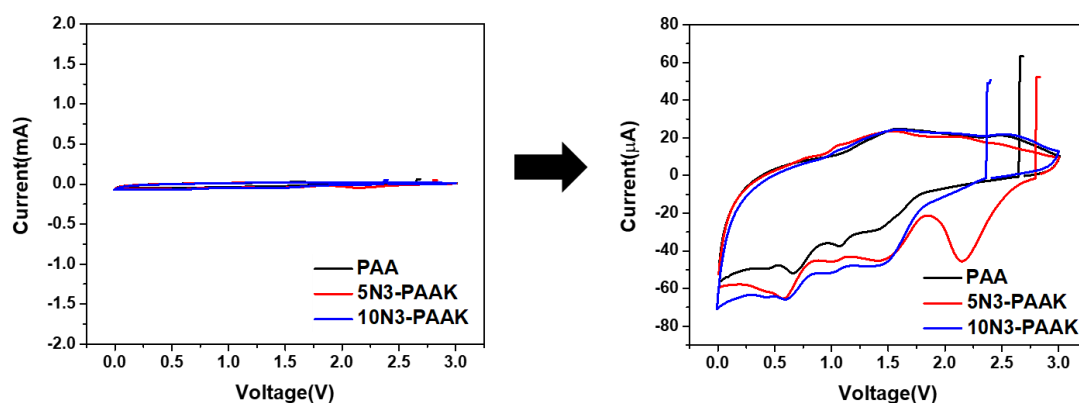


Figure 3.6 Cyclic voltammetry of PAA, 5N3-PAK, 10N3-PAK polymer film

As preliminary data, electrochemical performance of N3-PAAK-PVA polymer which ratio is 3:72:25 is tested in Figure 3.6. When the electrode is made by conventional method, it shows quite good ICE(90%). But it show fast capacity fading at initial cycle. Polyacrylat and polyvinylalcohol will not make any side reaction because usefulness of these polymer is already proved. because unreacted azide makes side reaction. So we think unreacted azide group can make side reaction with lithium deposition although it has only 3% azide group. When we check FT-IR data, we can see the azide functional group reaction condition. First, we try thermal treat according to temperature in order to use existing easy electrode preparation methodes (Figure 3.8 (a)). But it doesn't react at any high thermal condition like electrode dry, 150°C for 3hours in vaccum condition. So we can know that Figure 3.7 polymer of electrode cannot get any azide reaction with carbon material. Second, we try UV treat because azide is also can react by UV treat. If we use 365 nm UV, it show no any reaction. But UV treat with 254 nm can easily make azide reaction during short time with low power (6W) in Figure 3.8(b). After 30min with 254nm UV, 2106cm⁻¹ of azide peak has disappeared.

Before electrochemical performance, cyclic voltammetry is tested with UV treated polymers. Azide polymers are already tested that it has electrochemical stability in this voltage range. And when these are compared with UV-treated polymer electrode, UV-treated polymers show similar or fewer current range with smaller side reaction. So stability of polymers are proved by CV. And in order to make reaction of azide group, we treat UV to electrode (active material +polymeric binder+conductive material). But Figure 3.10(a) show very low ICE(5N3:80%, 10N3:60%). Because azide can react with conductive material, super P. So super P which react with azide polymer lose its electronic conductivity. So as the amount of azide is increased, it shows more low ICE. Also, when the ratio of azide in polymer is higher, electrode show lower ICE. But compared with Figure 3.7(b), it looks no azide side reaction.

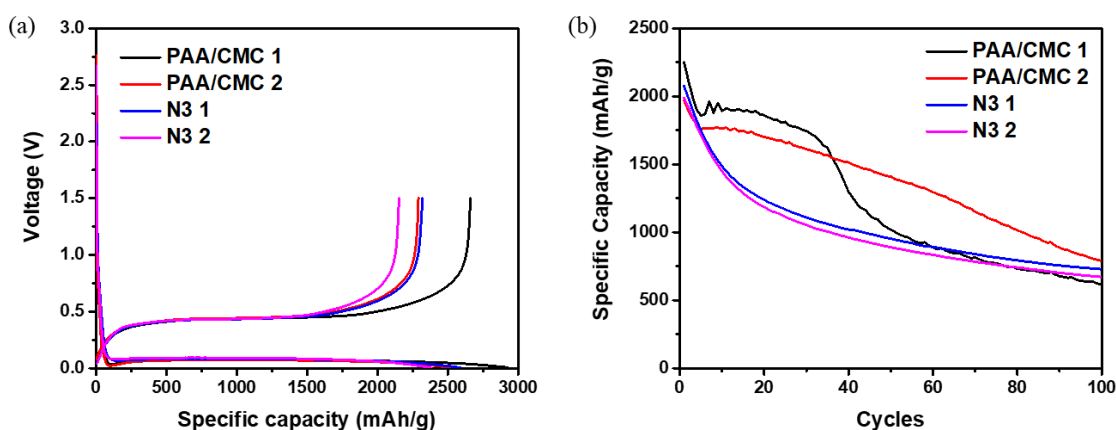


Figure 3.7 Electrochemical performance of azide polymer with PAA/CMC reference. (a) Voltage profile of initial cycle (b) cycle test

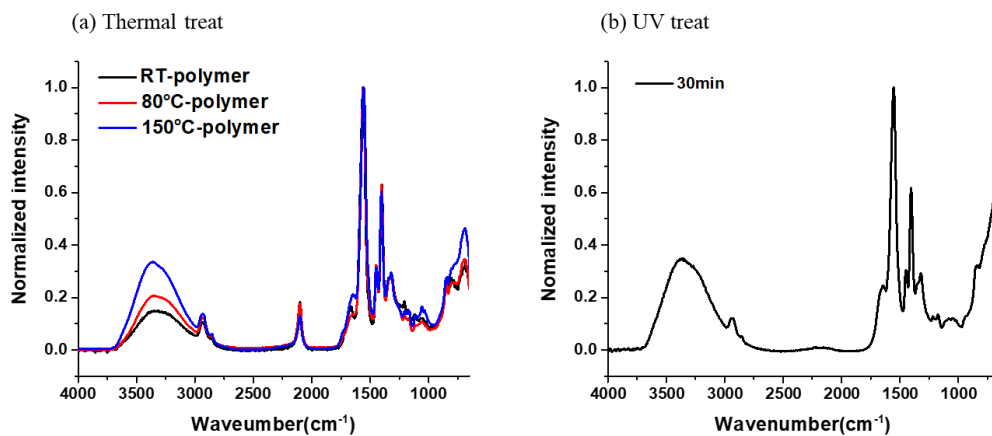


Figure 3.8 IR spectra of azide polymer of (a) thermal treat according to temperature and (b) UV treat

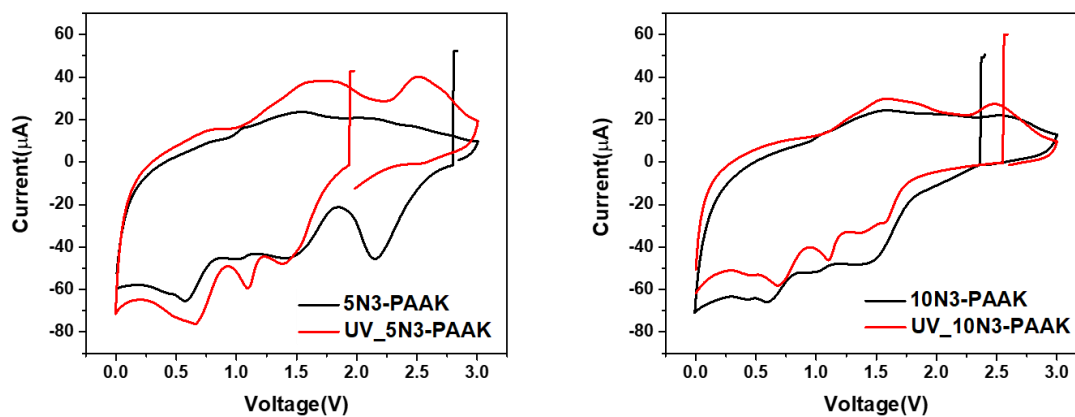


Figure 3.9 Cyclic voltammetry of UV treat or not treat azide polymer film

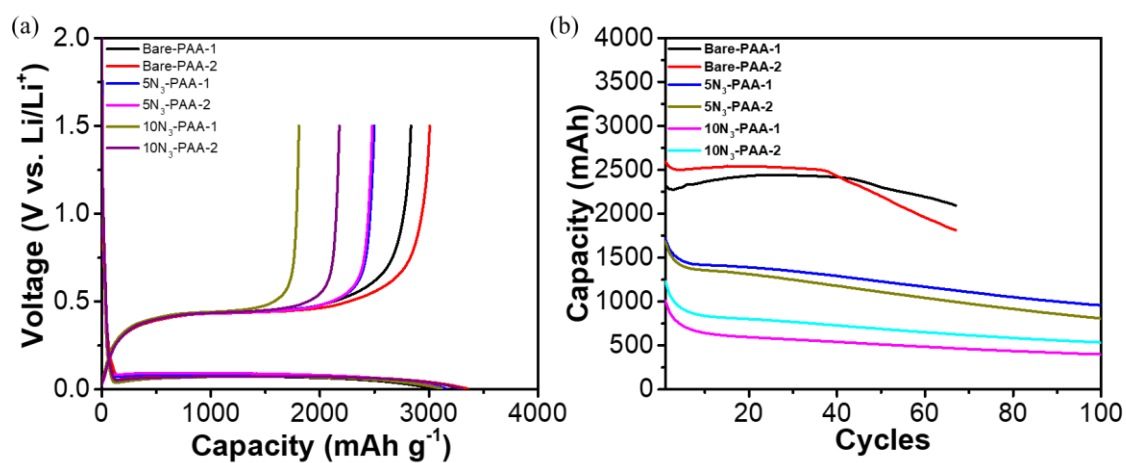


Figure 3.10 Electrochemical performance of UV treat electrode (a) initial voltage profile (b) cycle test

So we made polymer precoated active material by UV treat. Azide polymer decompose to nitrene and react with surface of carbon of silicon nanoparticle. The ratio of active material and coated polymeric binder is 8:1. Unreacted azide polymer can be removed by dissolving active material in water. Polymer which react with active material cannot dissolve in water. But unreacted polymer can dissolve in water so it can be separated by removing supernatant after ultracentrifuge. And the ratio can be confirmed by thermogravimetric analysis(TGA) at Figure 3.10. From weight at 100°C to the lowest weight, we can calculate the ratio of polymer and silicon. Over the 450°C, it show increased weight due to silicon nitride formation.

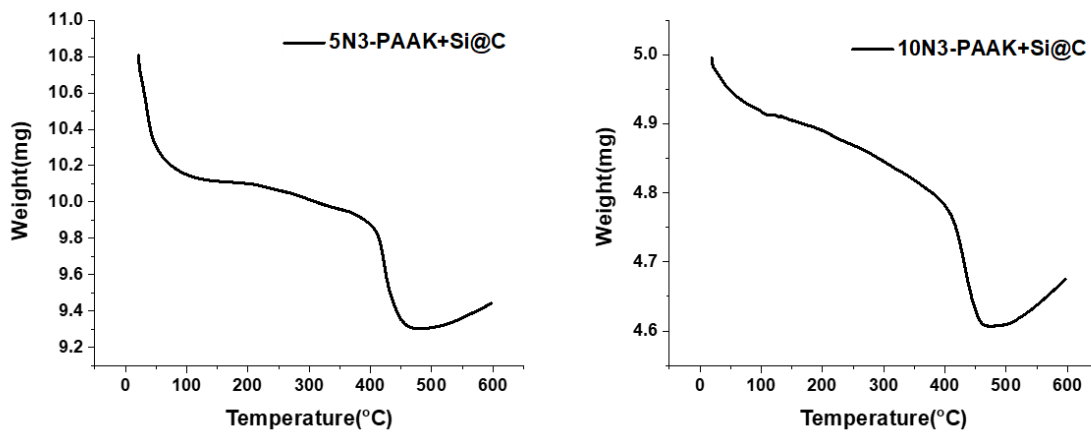


Figure 3.11 TGA graph for polymer coated Si@C. The ratio of polymer with active material is 1:8

After add conductive material, with ratio active material:Super-P 9:1, electrochemical performance is tested. It showed similar and quite high initial coulombic efficiency(5N3:81%, 10N3:83%) regardless of ratio of azide part in polymer (Figure 3.13). It is smaller ICE than reference PAA/CMC(90%) because coated polymer hinder the conductivity of active material. But both 5N3 and 10N3 polymer's cycle retention at 1 C-rate is much improved in polymer coated system(81~85% at 150cycles). Compared to PAA/CMC reference which has 30% retention efficiency at 150cycles with 0.2 C-rate, the rate retention of azide polymer is very big improvement. Also, usually high loading level make high resistance within the electrode and make fast capacity fading. But this system can make high retention efficiency in high loading level of electrode(1mg/cm²). Although both polymers show similar retention property, high ratio azide polymer show slightly higher retention efficiency. The polymer connection system is usefull for binding and maintaining electrode.

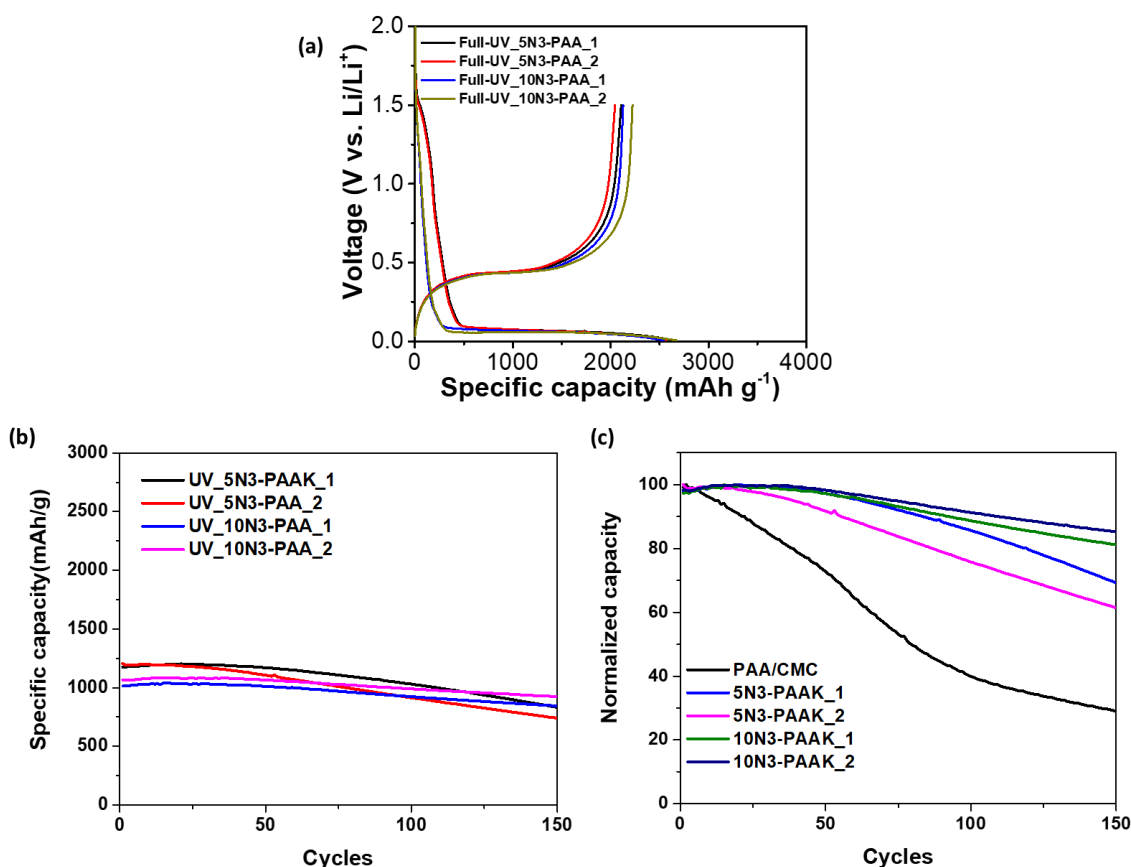


Figure 3.12 Electrochemical performance of azide polymer coated silicon electrodes. (a) Initial voltage profile (b) Cycle performance (c) Normalized data with PAA/CMC reference

Also we made electrode with CNT in order to see the effect of CNT with azide group. When the amount of CNT increased, azide effect also increase. First we prepared electrode with 1wt% CNT in electrode. The initial coulombic efficiency of these electrode show similar value regardless of ratio of azide in polymer(ICE=85%). And also, retention properties are similar and is higher than reference electrode. When the electrode is prepared with 2wt% CNT, high azide ratio polymer show less ICE(73.6~79%) and initial capacity. Although these show different initial capacity, all these electrodes has high capacity retention up to 100 cycles (64~70%). Also, it has enhanced cycle retention property in high loading level (1mg/cm²).

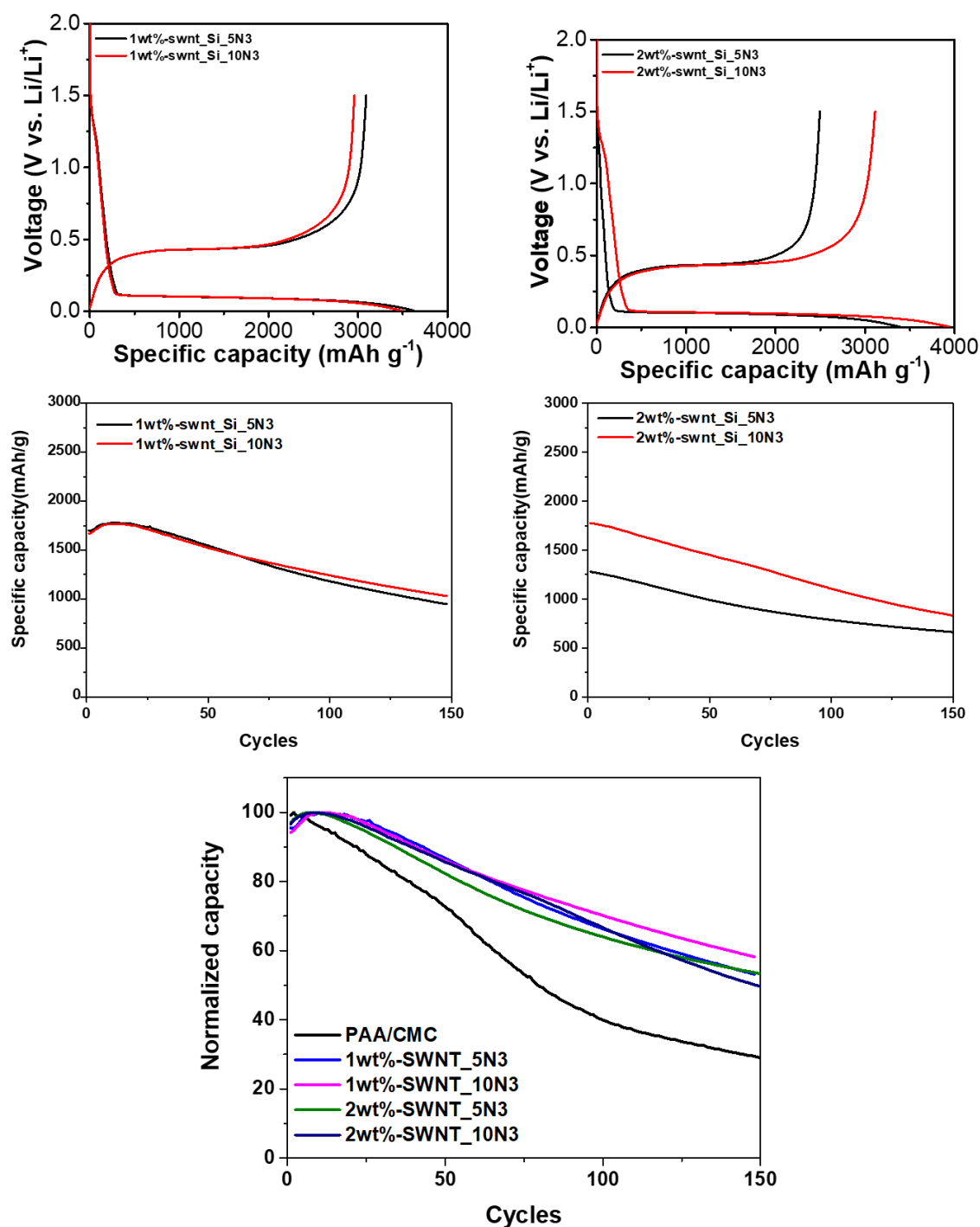


Figure 3.13 Electrochemical performance of azide polymer with SWNT. (a) Initial voltage profile with 1wt% SWNT (b) Initial voltage profile with 2wt% SWNT (c) Cycle performance with 1wt% SWNT (d) Cycle performance with 2wt% SWNT (e) Normalized capacity with reference PAA/CMC

In conclusion, we successfully synthesized new polymer which has azide functional group. Azide moiety can conjugate with carbon material and potassium polyacrylate moiety can increase the elasticity and adhesion property to current collector. Polymer is confirmed by NMR, IR and GPC. This polymer has enhanced elastic property. Also, we see the possibility and property of azide polymer as binder for lithium ion battery. Both electrode which used active material coated with polymer by UV and electrode with CNT have quite good ICE and high capacity retention property up to 1C-rate compared to PAA/CMC reference. Also this azide polymer can maintain and withstand in high loading level of electrode. So this polymer system can suggest new method to high loading level electrode and fast charging/discharging system.

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